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## D16

### ADVANCED TECHNOLOGY FOR DESTRUCTION OF WATERBORNE ORGANIC POLLUTANTS

Paul Skala and Harry Whittaker  
Engineering Section, Environmental Emergencies Technology Division,  
River Road Environmental Technology Centre, Ottawa, Ont. K1A 0H3.

and

Hussain Al-Ekabi<sup>1</sup>, Mike Robertson, Ali Safarzadeh-Amiri and  
Bob Henderson  
Nulite, A Division of Nutech Energy Systems Inc., 317 Consortium  
Court, London, Ontario N6E 2S8.  
Phone (519)668-7530 Fax (519)685-9800

#### ABSTRACT

Nulite is developing an advanced technology for water treatment. This technology uses  $\text{TiO}_2$  photocatalytic mineralization of organic pollutants into innocuous inorganic species. A prototype photoreactor consisting of a near UV lamp surrounded coaxially by a fibreglass mesh to which a thin layer of  $\text{TiO}_2$  (anatase) is firmly bonded was fabricated by Nulite. The Nulite reactor was tested on each individual as well as an equimolar mixture of all components of the Gloucester Landfill<sup>2</sup> water and found to be very efficient. The reactor results indicate that this technology will have wide application in the cleanup of organically contaminated waters since Gloucester water contains four different classes of the major concern organic pollutants.

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<sup>1</sup>correspondence should be addressed to this author

<sup>2</sup>Gloucester Landfill is a landfill site situated in the Township of Gloucester outside of Ottawa, Ontario. From 1968 - 1984, it has been the repository for chemical wastes from local laboratories.

## INTRODUCTION

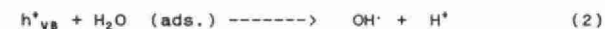
The presence of chlorinated hydrocarbons and other organic pollutants in natural and drinking waters has sparked much concern both in Europe and North America. While many of these pollutants are nonbiodegradable and persistent in the environment, some can be degraded by microbiological processes. However, microbial degradation requires a long period of time. In contrast, other methods are generally effective in removing organic pollutants from water, but most of them merely transfer the pollutants from a large volume of contaminated material into a smaller volume of concentrate which then requires expensive treatment or special dumping permits. Activated carbon treatment has been widely used to remove most organic compounds from such large volumes. However, the disposal of the spent carbon poses a severe problem as landfill sites come under increasing regulatory restrictions. Thus, an exhaustive search is currently underway for an alternative treatment of these concentrates and the original waters.

The photocatalytic mineralization of chlorinated hydrocarbons and other organic pollutants in water mediated by illuminated  $\text{TiO}_2$  has been demonstrated<sup>1-8</sup>. This approach represents a highly promising complete treatment since it would render all organic pollutants virtually harmless.

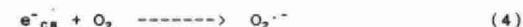
The illumination of  $\text{TiO}_2$  with light of wavelengths  $<400\text{nm}$  produces photoelectrons in the conduction band and positive holes in the valence band:



The hole ( $h^+_{\text{VB}}$ ) and electron ( $e^-_{\text{CB}}$ ) are both able to participate in chemical reactions. At the surface, the hole reacts with either adsorbed  $\text{H}_2\text{O}$  or with a surface hydroxyl group to form an hydroxyl radical which is a powerful oxidizing agent for organic pollutants.



Simultaneously, the molecular oxygen adsorbed on the surface will react with the electron to form superoxide ion ( $\text{O}_2^{\cdot-}$ ).



This process delays the electron/hole recombination and thus makes the degradation of the organic pollutants more efficient.

The  $\text{TiO}_2$  photocatalyst, in most of the earlier studies on the photocatalytic mineralization of organic pollutants, was freely suspended in aqueous solutions and thus filtration and resuspension of the photocatalyst are obvious practical problems. This prompted Nulite to build a prototype photoreactor in which the  $\text{TiO}_2$  (anatase) is firmly supported on a fibreglass mesh. This photoreactor could be used for both single-pass and multi-pass mode experiments.

The earlier studies on the  $\text{TiO}_2$ -mediated degradation of organic pollutants have dealt with the degradation of single organic compounds. It was, therefore, desirable to test the performance of the Nulite prototype reactor not only on a variety of single organic compounds but also on an equimolar mixture of Gloucester water components.

## EXPERIMENTAL

### The Nulite Prototype Photoreactor

The Nulite prototype photoreactor comprises a jacket, a lamp and a photocatalytic sleeve. The lamp emits ultraviolet light in the 300-400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh which is coated with a firmly bonded layer of titanium dioxide (anatase).

The anatase layer is activated by ultraviolet light. Contaminated water flows through the reactor in parallel with the lamp. As the water passes through the sleeve, the open pore configuration of the mesh creates turbulent mixing. In concert with the large surface area of the mesh, this mixing ensures contact between the organic pollutant and the photocatalyst.

The reactor was placed vertically and connected to a 4000 ml glass reservoir and a peristaltic pump. The flow of the recirculated solution through the system was controlled by changing the electrical input of the pump with a rheostat, and measured with a flow meter. All tubing used in connecting the apparatus was leach resistant teflon or viton.

### General Procedure

The Nulite prototype photoreactor was operated at constant temperature (27°C) by placing the reservoir into a suitable water bath. Typically, a standard volume (3000ml) of a solution of the desired contaminant of known concentration ( $5 \times 10^{-5} \text{M}$ ; 3.5-5ppm) was made up using HPLC grade water and good grade chemicals. This solution except for a small aliquot (about 5ml), was placed in the reservoir and pumped through the system, which had been previously washed with HPLC grade water and drained. As soon as the desired

flow rate and temperature were established a sample of the solution was taken, usually at the reactor inlet, and the UV light was turned on. Samples were then taken at regular intervals and analyzed by GC, while the solution was pumped through the system at controlled flow rate and temperature. The small aliquot, taken before the solution was transferred to the reservoir was analyzed and used as a standard to calibrate the GC detector's response to a given compound(s). The GC analyses of all samples were performed on a Hewlett Packard 5830A instrument, using a Megabore DB 1701 column (30m long, 0.4mm ID), flame ionization detector at 260°C, and direct injection of 1-2  $\mu\text{l}$  of sample. The injection port temperature was held at 260°C and helium (1.5ml/min) was used as carrier gas. Oven temperature varied depending on the particular needs of each compound or mixture, typically 150°C for phenol analysis, 40-80°C for most other organics. For the analysis of the equimolar mixture, the following temperature program was used: 1.5 min. initial hold at 20°C; 7°C/min (5 min); 15°C/min (7 min); 30°C/min until 210°C was attained.

## RESULTS AND DISCUSSION

### Degradation of Phenol

Initially, it was desirable to test the Nulite prototype reactor with a known  $\text{TiO}_2$  photocatalyzed mineralization reaction. The mineralization of phenol was chosen for a number of reasons: (1) earlier studies suggested that complete mineralization of phenol mediated by illuminated  $\text{TiO}_2$  is fairly fast, (2) being an aromatic compound, it represents one of the main classes of compounds for which the Nulite reactor was designed and (3) good solubility in water and low volatility allow easier sample manipulation and higher accuracy of kinetic measurements.

It is important, in a flow solid-liquid reaction, to determine the extent to which mass transfer may affect the overall rate of mineralization in the Nulite reactor and to establish a kinetic region in which the mass transfer is sufficiently rapid to have no noticeable effect on the rate of the overall degradation process. Thus, the degradation of phenol (5 ppm) in aerated aqueous solutions *vs* irradiation time was investigated at different flow rates. The results indicated that the flow rate has little effect on the overall rate of phenol degradation between 0.05 and 0.25 gpm but has no effect between 0.25 and 0.5 gpm where the rate of degradation seems to be constant within the limits of the accuracy of the GC analysis. Therefore, the limit of the kinetic region is found to be around 0.25 - 0.5 gpm for the degradation of 5 ppm of phenol. Since other organic compounds may, in principle, be mineralized faster than phenol, the flow rate of 0.5 gpm was used for all subsequent kinetic measurements.

Figure 1 illustrates the degradation of phenol (5 ppm) in aerated aqueous solution as a function of irradiation time. The degradation proceeds very efficiently. Plots of  $\ln(C_0/C)$  *vs* irradiation time shows good linearity indicating that the reaction approximates first order kinetics to a high degree of degradation (>80%). The apparent rate constant is found to be  $0.067 \text{ min}^{-1}$ . This behaviour could be rationalized in terms of a modified form of the Langmuir-Hinshelwood (L-H) kinetic treatments which has been used successfully to describe many solid-liquid reactions<sup>9</sup>.

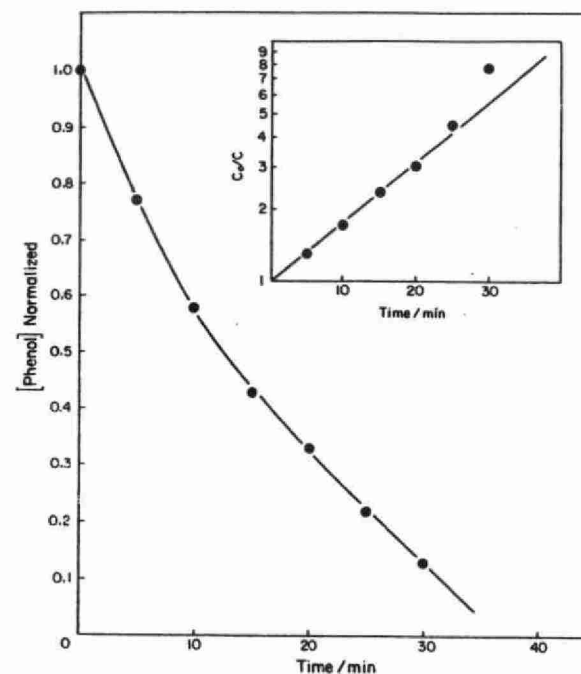


Figure 1. Plot showing changes in the concentrations of phenol as a function of irradiation time. The insert is a plot of  $\ln(C_0/C)$  *vs* time.

According to the L-H kinetic treatment, a unimolecular surface reaction, where the reactant is significantly more strongly adsorbed than the product, will obey an equation of the form:

$$\text{Rate} = -dC/dt = k_r \theta = k_r [KC_o / (1 + KC_o + K_w C_w)] \quad (5)$$

where  $k_r$  is the reaction rate constant,  $\theta$ , is the fraction of the surface covered by the reactant (contaminant),  $C_o$  is the initial concentration of the organic reactant in solution,  $K$  is the adsorption coefficient of the reactant,  $K_w$  is the adsorption coefficient of water and  $C_w$  is the concentration of water (55.5M).

Similarly, a bimolecular reaction between two surface species (without significant mutual displacement) obeys equation (6)

$$\text{Rate} = k_r \theta_1 \theta_2 \quad (6)$$

where  $\theta_1$  and  $\theta_2$  are the fractions of the surface covered by the surface reactant species. Equation (6) reduces to a form similar to that of equation (5) where the concentration of one of the species remains constant. Since the concentration of the reactive species (OH radical) remains constant (the light intensity and the amounts of  $TiO_2$  and water are kept constant), equation (5) can be adapted to explain our results.

Since the concentration of water  $C_w$  is much greater than the solute  $C_o$ , and  $C_w$  remains essentially constant, the part of  $TiO_2$  surface covered by the solvent (water) is approximately constant at all the reactant concentrations used.

Integration of equation (5) gives equation (7).

$$\ln(C_o/C) + (K/(1+K_w C_w)) (C_o - C) = (k_r K / (1+K_w C_w)) t \quad (7)$$

Obviously, equation (7) is the sum of zero-order and first-order rate equations and their contribution to the overall reaction depends essentially on the initial concentrations  $C_o$ . When  $C_o$  is very low, equation (7) reduces to equation (8) which is a first-order rate equation.

$$\ln(C_o/C) = k' t \quad (8)$$

where  $k'$  is the apparent first-order rate constant. Equation (8) explains the results presented in this paper.

#### Degradation of the Gloucester Water Components

The main objective of this study was not only to test the performance of the Nulite prototype reactor on one particular sample of contaminated water, but also to compare rates of degradation of various compounds with different functional groups and possibly relate the rates of degradation of each compound to its structure.

GC analysis of the Gloucester water sample revealed 12 main organic contaminants (Table 1). Therefore, it was considered important in this context to determine the reactor's potential preference for some classes of compounds. The sample of Gloucester landfill water contains at least one compound of each of the main classes that one considered the most likely targets of an industrial application of the Nulite reactor.

Table 1

Organic contaminants in Gloucester ground water and RO concentrate.

COMPOUNDS	FEED/ppm	CONCENTRATE/ppm
Benzene	1.177	9.570
Toluene	0.204	1.528
Chlorobenzene	0.008	0.025
1,1-Dichloroethylene	0.010	0.050
1,2-Dichloroethylene	-----	-----
Trichloroethylene	0.417	2.091
Diethylether	0.273	1.986
Tetrahydrofuran	-----	-----
1,1-Dichloroethane	0.126	0.792
1,2-Dichloroethane	0.128	0.748
1,1,1-Trichloroethane	0.145	1.117
Chloroform	0.338	2.313

For this reason, it provided an ideal model for the first trial of the reactor. Also, the knowledge of the reactor's selectivity towards all components of this mixture is likely to become a valuable tool in later predictions of degradation rates of related compounds. Thus, first it was important to investigate the individual degradation of all compounds involved plus tetrahydrofuran which was included at this stage in order to provide more reference data on the degradation of ethers. The next stage was the treatment of an equimolar mixture of all compounds except tetrahydrofuran which interfered with the GC analysis of 1,1,1-trichloroethane.

To simplify the discussion, the Gloucester water components are divided into four different classes of pollutants. They are: (1) aromatic compounds, (2) chlorinated ethylenes, (3) ethers and (4) chlorinated alkanes. The degradation data of the components of each class of pollutants are presented separately.

#### Degradation of the Aromatic Compounds of the Gloucester Water

The individual degradation of aerated aqueous solutions of benzene, toluene and chlorobenzene was investigated using the Nulite reactor and found to be very efficient. Figure 2 shows the degradation of toluene as a function of irradiation time. The reaction follows first-order kinetics as a straight line was obtained when  $\ln(C_0/C)$  was plotted vs irradiation time. The apparent rate constant was  $0.072 \text{ min}^{-1}$ . The degradation of benzene and chlorobenzene also follows first-order kinetics with apparent rate constants of  $0.071$  and  $0.052 \text{ min}^{-1}$ , respectively. Clearly, the degradation rate constants of toluene and benzene are higher than that of chlorobenzene. The OH radical is known to have an electrophilic character<sup>10</sup> and thus it would be, generally, expected that aromatic compounds substituted with an electron donating group are more readily attacked than those substituted with an electron withdrawing group such as Cl.

#### Degradation of the Chlorinated Ethylenes of the Gloucester Water

The individual degradation of aerated aqueous solutions of 1,1-dichloroethylene, 1,2-dichloroethylene and trichloroethylene was investigated as a function of irradiation time. The degradation of all three compounds was very efficient. The data for



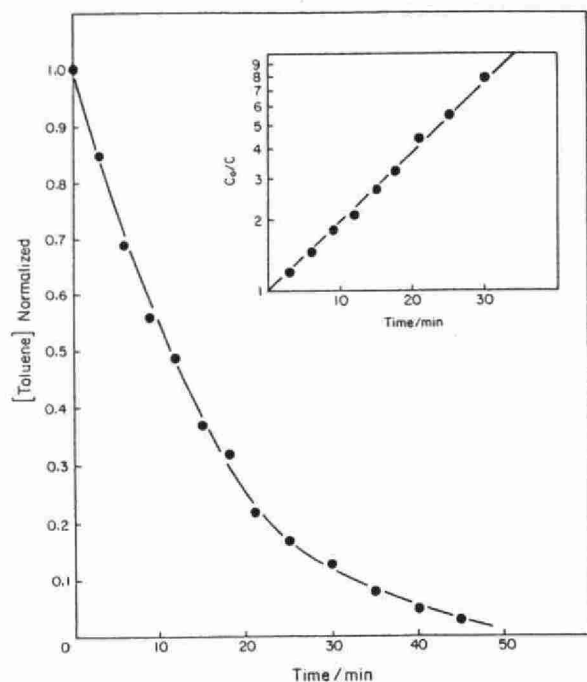


Figure 2. Plot showing changes in the concentrations of toluene as a function of irradiation time. The insert is a plot of  $\ln(C_0/C)$  vs time.

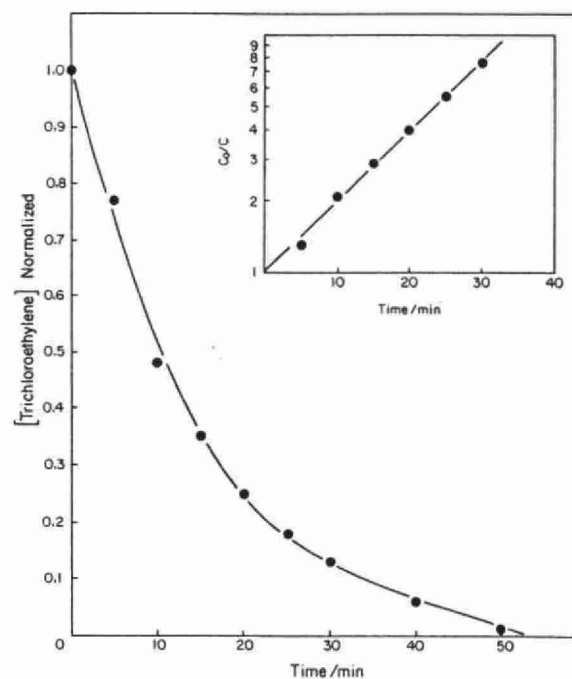


Figure 3. Plot showing changes in the concentrations of trichloroethylene as a function of irradiation time. The insert is a plot of  $\ln(C_0/C)$  vs time.

trichloroethylene are shown in Figure 3. The reaction follows first-order kinetics with an apparent rate constant of  $0.069 \text{ min}^{-1}$ . The rate constants for degradation of 1,1-dichloroethylene and 1,2-dichloroethylene are  $0.083$  and  $0.05 \text{ min}^{-1}$ , respectively.

#### Degradation of the Ethers of the Gloucester Water

Although tetrahydrofuran was not present in the Gloucester water sample, it was included in this study for two reasons: (1) it had been previously found in other Gloucester water samples taken from other sites and (2) it provides more reference data on degradation of ethers. Thus, the photocatalytic degradation of tetrahydrofuran and diethylether in aerated aqueous solutions was investigated. The degradation of both compounds was efficient and follows first-order kinetics with apparent rate constants of  $0.048$  and  $0.052 \text{ min}^{-1}$  for tetrahydrofuran and diethylether, respectively. Figure 4 demonstrates the degradation of diethylether as a function of irradiation time.

It is noteworthy that the degradation rates of tetrahydrofuran and diethylether are comparable with those of aromatic compounds and chlorinated ethylenes. Diethylether and tetrahydrofuran are known to be good hydrogen donating compounds and thus abstraction of their  $\alpha$ -hydrogen atoms by OH radical is expected to be fast. This would render the degradation high efficient.

#### Degradation of the Chlorinated Alkanes of the Gloucester Water

Unlike the degradation of the aromatic compounds, the chlorinated ethylenes and the ethers, the degradation of 1,2-dichloroethane, chloroform and 1,1,1-trichloroethane under similar conditions was considerably slower. However, complete degradation could be achieved with longer irradiation time. The degradation

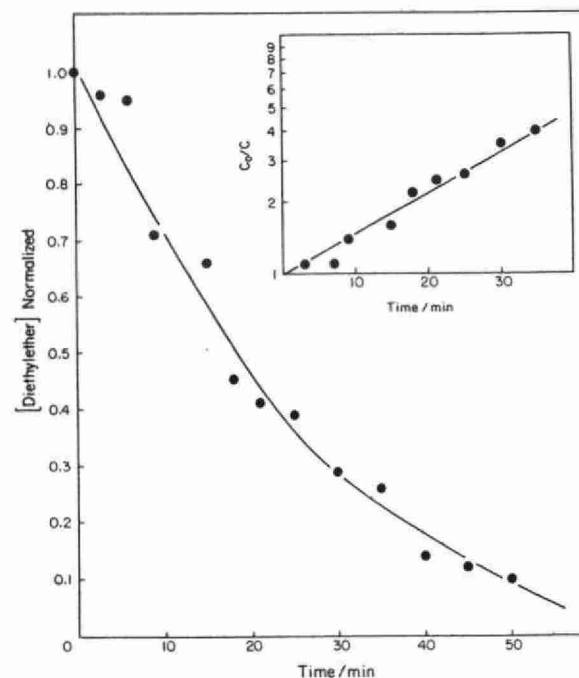


Figure 4. Plot showing changes in the concentrations of diethylether as a function of irradiation time. The insert is a plot of  $\ln(C_0/C)$  vs time.

for all three cases follows first-order kinetics and the data for 1,2-dichloroethane are depicted in Figure 5. The degradation rate constants for chloroform, 1,2-dichloroethane and 1,1,1-trichloroethane were 0.01, 0.014 and 0.01 min<sup>-1</sup>, respectively. Clearly, the rates of degradation of the chlorinated ethylenes are higher than those of the chlorinated alkanes. Alkanes are known to be less reactive towards OH radical attack than alkenes.

#### Degradation of an Equimolar Mixture of the Gloucester Water Components

Having investigated individually the photocatalytic degradation of the Gloucester water components, it was important to test the degradation of an equimolar mixture of the Gloucester water components in Nulite's reactor. In this regard, it should be mentioned that most of the reports so far published on the TiO<sub>2</sub>-mediated mineralization of organic pollutants have dealt with the degradation of single organic compounds. Thus, the degradation of an equimolar mixture (2.5x10<sup>-5</sup>M; 1.75-2.5ppm each) of benzene, toluene, chlorobenzene, diethylether, 1,1-dichloroethylene, 1,2-dichloroethylene, trichloroethylene, 1,2-dichloroethane, chloroform and 1,1,1-trichloroethane in aerated aqueous solution was carried out as a function of irradiation time. In agreement with the individual degradation data, the results illustrated in Figure 6 clearly show that benzene, toluene, chlorobenzene, 1,1-dichloroethylene, 1,2-dichloroethylene, trichloroethylene and to a lesser extent, diethylether degrade with comparable rates. Approximately 100 min. was enough to degrade completely these components. By contrast, and in agreement with the individual degradation data, the degradation of chloroform, 1,2-dichloroethane and 1,1,1-trichloroethane was much slower. However, their degradation became faster once the other components had been degraded.

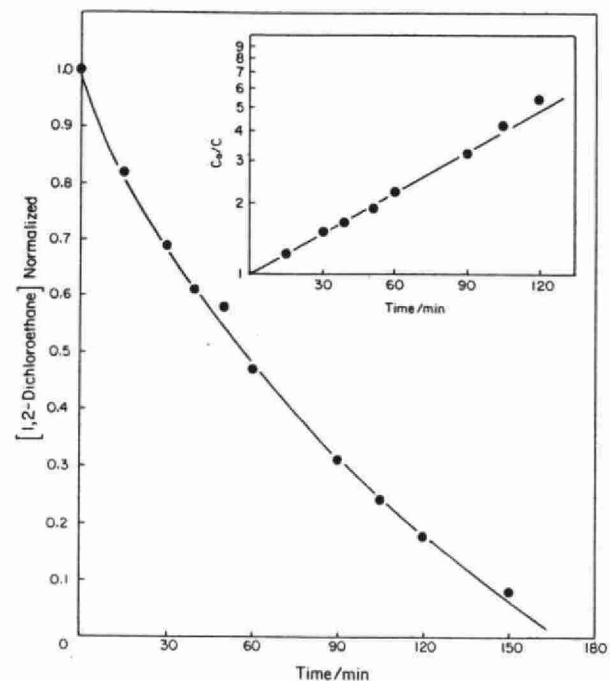


Figure 5. Plot showing changes in the concentrations of 1,2-dichloroethane as a function of irradiation time. The insert is a plot of  $\ln(C_0/C)$  vs time.

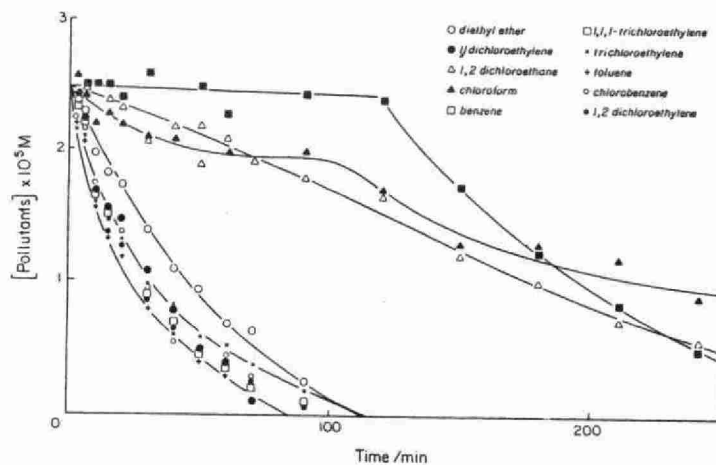


Figure 6. Plot showing changes in the concentrations of an equimolar mixture of Gloucester water components as a function of irradiation time.

It is noteworthy that the degradation of all compounds in this equimolar mixture followed first-order kinetics. Representative plots of  $\ln(C_0/C)$  vs time for benzene, 1,2-dichloroethylene and 1,2-dichloroethane are presented in Figure 7 and the apparent rate constants for all the degraded components are presented in Table 2 along with the individual degradation rate constants.

Table 2

Apparent first-order rate constants  $k'$  and  $t_{1/2}$  for the degradation of Gloucester water components in a continuous recirculation mode at 0.5 gpm flow rate.

Compound	Individual		Mixture	
	$k' \times 10^3, \text{min}^{-1}$	$t_{1/2}, \text{min}$	$k' \times 10^3, \text{min}^{-1}$	$t_{1/2}, \text{min}$
Benzene	71	9.8	33	21.0
Toluene	72	9.6	37	18.7
Chlorobenzene	52	13.3	31	22.4
1,1-Dichloroethylene	83	8.4	29	23.9
1,2-Dichloroethylene	50	13.9	29	23.9
Trichloroethylene	69	10.0	30	23.1
Diethylether	52	13.3	20	34.7
Tetrahydrofuran	48	14.4	--	----
Chloroform	10	69.3	5	138.6
1,2-Dichloroethane	14	49.5	4	173.3
1,1,1-Trichloroethane	10	69.3	--	----

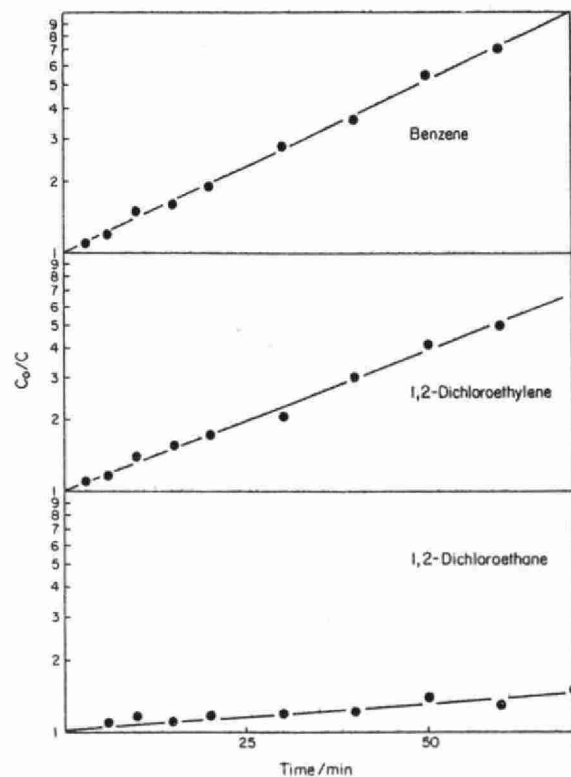


Figure 7. Plot of  $\ln(C_0/C)$  vs time for benzene, 1,2-dichloroethylene and 1,2-dichloroethane of the Gloucester water mixture.

## CONCLUSIONS

- 1) The Nulite prototype photoreactor degraded with high efficiencies all components of the Gloucester water both individually and in an equimolar mixture. Clearly, this is an advanced step in the degradation of organic pollutants via heterogeneous photocatalysis since all of the  $\text{TiO}_2$ -mediated degradation studies so far published have dealt only with the degradation of single organic compounds. The degradation of the Gloucester water components by the Nulite reactor acquires special importance not only because of the large number of organic pollutants tested individually or in an equimolar mixture but also because of the diverse nature of the organic compounds involved. The Gloucester water contains organic compounds belonging to different classes of organic pollutants which are of the greatest environmental concern today.
- 2) The Nulite reactor degraded the aromatic compounds, (both chlorinated and unchlorinated), the chlorinated ethylenes and diethylether of the Gloucester water with high efficiencies while the rates of degradation of the chlorinated alkanes were considerably slower. Since virtually any treatment of a real mixture of contaminants is in fact a case of competitive degradation where different compounds (contaminants) compete with each other for the photocatalyst, the selectivity of the photocatalyst in such cases is an important factor. A reactor capable of oxidizing primarily the compounds of most concern, even in the presence of a high concentration of other compounds, would have a definite advantage over one that either did not discriminate or treated the most noxious substances last, with minimum efficiency, or not at all.



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- 3) Although the Nulite reactor showed remarkable degradation efficiencies towards Gloucester water which contains four different classes of organic pollutants, it should be noted that the reactor is an early stage prototype and work is in progress to optimize its degradation capacity.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Carey, J.H.; Lawrence, J.; Tosine, H.M., Bull. Environ. Contam. Toxicol., 1976, **16**, 697.
2. (a) Hsiao, C.-Y.; Lee, C.-L.; Ollis, D.F., J. Catal., 1983, **82**, 418. (b) Pruden, A.L.; Ollis, D.F., Environ. Sci. Technol., 1983, **17**, 628. (c) Pruden, A.L.; Ollis, D.F., J. Catal., 1983, **82**, 404 (d) Ollis, D.F., Hsiao, C.-Y.; Budiman, L.; Lee, C.L., J. Catal., 1984, **88**, 89. (e) Nguyen, T.; Ollis, D.F.; J. Phys. Chem., 1984, **88**, 3386. (f) Ollis, D.F., Environ. Sci. Technol., 1985, **19**, 480. (g) Ollis, D.F., J. Catal., 1986, **97**, 5693.
3. (a) Matthews, R.W., J. Chem. Soc. Faraday Trans. 1, 1984, **80**, 457. (b) Matthews, R.W., J. Catal., 1986, **97**, 565. (c) Matthews, R.W., Water Res., 1986, **20**, 569. (d) Matthews, R.W., J. Phys. Chem., 1987, **91**, 3328. (e) Matthews, R.W., Solar Energy, Chem., 1987, **38**, 405. (f) Matthews, R.W., Aus. J. Chem., 1987, **40**, 667.
4. (a) Barbeni, M.; Pramauro, E.; Pelizzetti, E.; Borgarello, E.; Gratzel, M.; Serpone, N., Nouv. J. Chim., 1984, **8**, 547. (b) Hidaka, H.; Kubota, H.; Gratzel, M.; Serpone, N.; Pelizzetti, E., Nouv. J. Chim., 1985, **9**, 67 (c) Hidaka, H.; Kubota, H.; Gratzel, M.; Delizzetti, E.; Serpone, N., J. Photochem., 1986, **35**, 219. (d) Pelizzetti, E.; Borgarello, M.; Minero, C.; Pramauro, E.; Serpone, N., Chemosphere, 1988, **17**, 499. (e) Barbeni, M.; Morello, M.; Pramauro, E.; Pelizzetti, E.; Vincenti, M.; Borgarello, E.; Serpone, N., Chemosphere, 1987, **16**, 1.165 (f) Al-Ekabi, H.; Serpone, N., J. Phys. Chem., 1988, **92**, 0000.
5. (a) Okamoto, K.; Yamamoto, Y.; Tanaka, H.; Tanaka, M., Bull. Chem. Soc. Jpn., 1985, **58**, 2015. (b) Okamoto, K.; Yamamoto, Y.; Tanaka, H.; Itaya, A., Bull. Chem. Soc. Jpn., 1985, **58**, 2023.
6. (a) Kraeutler, B.; Bard, A.J., J. Amer. Chem. Soc., 1978, **100**, 5985. (b) Izumi, I.; Dunn, W.W.; Wilbourn, K.O.; Fan, F.R.F.; Bard, A.J., J. Phys. Chem., 1980, **84**, 3207.
7. Oosawa, Y., J. Phys. Chem., 1984, **88**, 3069.
8. Herrman, J.-M.; Mozzanega, M.-N.; Pichat, P., J. Photochem., 1983, **22**, 333.
9. (a) Draper, A.M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V., J. Am. Chem. Soc., 1984, **106**, 6222. (b) Al-Ekabi, H.; de Mayo, P., J. Phys. Chem., 1985, **89**, 5815. (c) Al-Ekabi, H.; de Mayo, P., J. Phys. Chem., 1986, **90**, 4075. (d) Al-Ekabi, H.; de Mayo, P., Tetrahedron, 1986, **42**, 6277. (e) Hasegawa, T.; de Mayo, P., Langmuir, 1986, **2**, 362.
10. Anbar, M.; Meyerstein, D.; Neta, P., J. Phys. Chem., 1966, **70**, 2660.